# Roles of nano-sized Au in the reduction of $NO_x$ by propene over $Au/TiO_2$: An in situ DRIFTS study

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## ARTICLE INFO

## ABSTRACT

A mechanistic study of the selective catalytic reduction (SCR) of $NO_x$ by $C_3H_6$ has been investigated over nano-sized $Au/TiO_2$ catalyst using in situ diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS). The formation and consumption of adsorbed species on the catalyst surface have been intensively studied during co-adsorption of reactants and reaction condition. The presence of nano-sized Au particles played an important role in the formation of oxygenated hydrocarbons, especially acetate species. Importantly, Au active sites were crucial to the formation of isocyanate intermediate compounds and contributed to the conversion of these intermediates to $N_2$. The reaction mechanism of SCR over $Au/TiO_2$ has been discussed on the basis of DRIFTS results.

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## 1. Introduction

In the concerns of energy crisis and global warming, lean-burn engines, which work at high air/fuel ratio, are essentially promising for automobile industry because of their high fuel efficiency, and low $CO_2$ emission. However, these engines produce exhaust containing a large excess of oxygen making the commercial three-way catalyst (TWC) impossible for $NO_x$ reduction [1,2]. Thus, the reduction of $NO_x$ emission from lean-burn engine exhaust remains a challenge to both academic research and the automobile industry.

Researchers have reported the possibility of applying nano-sized gold catalysts for the selective catalytic reduction of $NO_x$ by hydrocarbons (HC-SCR). For example, Ueda et al. [3–5] reported that supported gold catalysts are active for reduction of NO with hydrocarbons (propene, propane, ethane, and ethene) in the presence of moisture and excess oxygen. Among different metal oxide supports, $Al_2O_3$ exhibited the highest conversion of NO to $N_2$ [3]. Since then, other research groups focused on the development of $Au/Al_2O_3$ catalysts for HC-SCR [6–9]. However, the disadvantage of $Au/Al_2O_3$ is that it is effective at quite high reaction tempera-

tures which are not favorable for treatment of diesel exhaust [3,6,7]. Moreover, the drawback of using support $Al_2O_3$ is the deactivation caused by $SO_2$ originating from fuel [10,11]. On the other hand, $TiO_2$ is a promising alternative support since the sulfation of $TiO_2$ in a $SO_2$ atmosphere is difficult [12], and this sulfur-resistant support has been widely used for the $NO_x$ selective catalytic reduction by $NH_3$ ($V_2O_5/TiO_2$) [13]. However, there is not much attention given to the HC-SCR activity of the $TiO_2$ supported gold catalysts.

Mechanisms of HC-SCR by $Al_2O_3$ supported nano-sized Au catalysts were proposed in a few publications [3,8]. Ueda's group suggested that the formation of $NO_2$ by the oxidation of NO with $O_2$ may be the first and slowest step followed by the reaction of $NO_2$ with $C_3H_6$. In situ diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) was used in research of Bamwenda et al. over $Au/\gamma$-$Al_2O_3$ catalyst [8]. The oxidation of NO to $NO_2$ is a prerequisite step followed by coupling of the $NO_2$ or its adspecies ($NO_x^-$) with activated $C_3H_6$ on active site on $Al_2O_3$ to form $C_nH_mN_xO_y$ species, such as –NCO or –CN, which are responsible for the propagation step. Their subsequent internal rearrangement and decomposition lead to the formation of $N_2$ and other products. However, there is no report to date about mechanism of SCR by propene over $Au/TiO_2$ catalyst, which performed better catalytic activity than $Au/Al_2O_3$ at low temperatures [14,15]. The present study concentrates on the investigation of roles of nano Au particles in the SCR reaction, especially in the formation and consumption of adsorbed species on $Au/TiO_2$ by using in situ DRIFTS. A proposed reaction mechanism based on DRIFTS results is also discussed.

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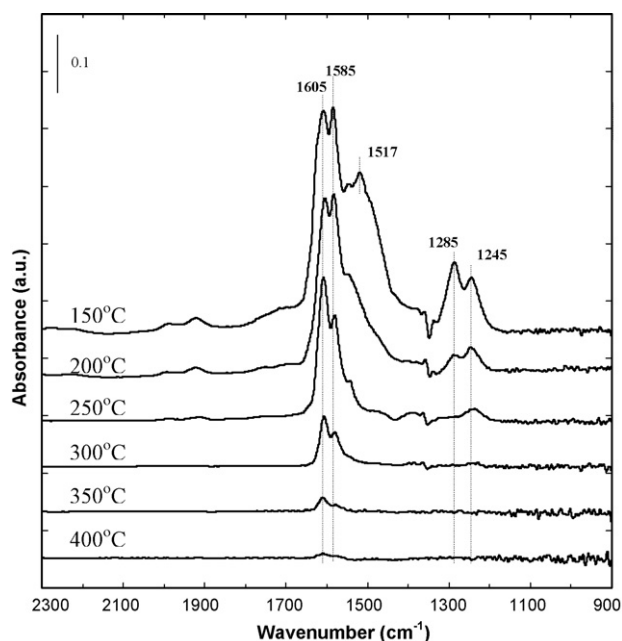
**Fig. 1.** DRIFTS spectra of adsorbed species over Au/TiO$_2$ after exposing in the flow of NO + O$_2$ for 40 min at different temperatures. Conditions: NO = 1500 ppm, O$_2$ = 10%.

## 2. Experimental

The Au/TiO$_2$ catalysts were prepared from JRC-TiO-7 (a reference catalyst of the Catalysis Society of Japan, 100% anatase) and HAuCl$_4$·4H$_2$O (99.9%, Wako Co.) by metal–sol method using polyvinyl alcohol (PVA) as describe elsewhere [14]. In brief, a freshly prepared solution of NaBH$_4$ was slowly added dropwise into the solution containing HAuCl$_4$ and PVA (weight ratio PVA/Au = 1). The JRC-TiO-7 was added after the pH was adjusted to 6.0 using ammonia solution. After washed, and dried at 100 °C overnight, the catalysts were calcined at 550 °C for 4 h. The average Au particle size on TiO$_2$ support was about 5.0 nm with 60% particles in the size of 3–5 nm as determined from transmission electron microscopy (TEM) using JEM-2010F (JEOL Ltd.) [14]. For comparison, the fresh JRC-TiO-7 support was calcined at 550 °C for 4 h and referred as TiO$_2$. The BET surface areas of the TiO$_2$ and Au/TiO$_2$, which were measured by Autosorb-1 (Quantachrome Instrument Corp.), were 115 and 102 m$^2$/g, respectively [15].

In the DRIFTS measurement, Au/TiO$_2$ containing 1 wt.% Au was mainly used. The sample powder (approximately 20 mg) was placed in a diffuse reflectance cell (DR-600Bi, Jasco corp.) which was coupled with a temperature controller. The cell was fitted by a KBr window at the top. Infrared spectra were recorded with a JASCO FT/IR-6100FV using a MCT-M detector cooled by liquid N$_2$. A total of 64 scans were accumulated at a resolution of 4 cm$^{-1}$ in different temperatures ranging from 150 to 400 °C. Prior to each experiment, the sample was pretreated in situ at 500 °C in helium stream (100 ml/min) for 30 min, followed by cooling to the desired temperature and then stabilizing for 30–60 min. The spectrum at this stage was collected and used as the background for other spectra at the corresponding temperature. Various gas mixtures were fed in situ to the catalyst at the same flow-rate of 100 ml/min. The concentrations (if presented) of NO, NO$_2$, C$_3$H$_6$, and O$_2$ in the gas mixture were 1500 ppm, 1500 ppm, 1500 ppm, and 10%, respectively, with He as a balance. The adsorption of each reactant has been carefully carried out at different temperatures to understand the adsorbed-species formation. The surface adsorbed species during the C$_3$H$_6$-SCR of NO over Au/TiO$_2$ catalyst at different temperatures were clarified by both simultaneously feeding and consecutive feeding of the reactants.

## 3. Results and discussion

### 3.1. Formation of adsorbed species during co-adsorption of reactants

The DRIFTS spectra obtained after the Au/TiO$_2$ catalyst was exposed to NO/O$_2$ for 40 min at various temperatures are reported in Fig. 1, in which assignment of the absorbance bands was listed in Table 1. Bands of bridging nitrate (1605, and 1245 cm$^{-1}$), bidentate nitrate (1585, and 1285 cm$^{-1}$), monodentate nitrate (at 1517, and 1285 cm$^{-1}$) were observed. Monodentate species were only detected at 150 °C while bridging and bidentate species were observed at all temperatures. When the exposing temperature was increased, the intensities of nitrate bands were decreased, especially from 300 °C. Comparison of DRIFTS spectra between TiO$_2$ and Au/TiO$_2$ after exposing to NO/O$_2$ for 40 min is shown in Fig. 2. The results at 200 and 300 °C were reported. We obtained almost similar spectra for both samples at each temperature. Thus, the adsorbed species during NO/O$_2$/He exposure were formed by and located on the TiO$_2$ support. The Au particle did not contribute to the formation of nitrate adsorbed species.

**Table 1**
Wavenumbers and assignment of adsorption bands in DRIFTS spectra.

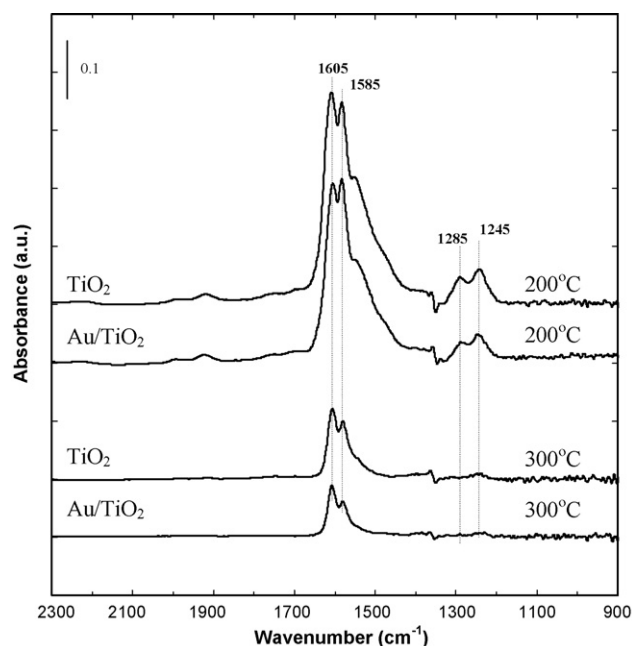| Wavenumber (cm$^{-1}$) (this work) | Surface species | Interpretation | Wavenumber (cm$^{-1}$) (literature) | Reference |
|---|---|---|---|---|
| 1605 | Bridging NO$_3^-$ (M–O)$_2$=NO | $\nu_s$(ONO) | 1607–1611 | [16] |
| 1245 | | $\nu_{as}$(ONO) | 1252–1258 | |
| 1580–1585 | Bidentate NO$_3^-$ (M–O$_2$NO) | $\nu_s$(ONO) | 1582–1589 | [16,17] |
| 1285 | | $\nu_{as}$(ONO) | 1296–1298 | |
| 1517 | Monodentate NO$_3^-$ (M–O–NO$_2$) | $\nu_s$(ONO) | 1510–1513 | [16] |
| 1285 | | $\nu_{as}$(ONO) | 1296–1298 | |
| 2956 | H–COO$^-$ | $\nu_{as}$(COO) + $\delta$(CH) | 2957 | [18] |
| 2875 | | $\nu_s$(CH) | 2873 | |
| 1550 | | $\nu_{as}$(COO) | 1554 | |
| 1381 | | $\delta$(CH) | 1381 | |
| 1360 | | $\nu_s$(COO) | 1360 | |
| 2986, 2936 | CH$_3$–COO$^-$ | $\nu$(CH) | 2984–2987, 2936 | [18–21] |
| 1550 | | $\nu_{as}$(COO) | 1540 | |
| 1440 | | $\nu_s$(COO) | 1440 | |
| 2978, 2936 | CH$_3$–CO–CH$_3$ | $\nu$(CH) | 2973, 2931 | [22] |
| 1675 | | $\nu$(C=O) | 1702 | |
| 1718 | CH$_3$–CHO | $\nu$(C=O) | 1718 | [23] |
| 2291–2262 | –CN | $\nu$(Ti–C≡N) | 2317–2234 | [22,24,25] |
| 2175–2202 | –NCO | $\nu_{as}$(Ti–N=C=O) | 2174–2209 | [25,26] |
| 1645 | –OH of H$_2$O | $\delta$(OH) | 1635–1650 | [22] |

**Fig. 2.** Comparison spectra of surface adsorbed species between Au/TiO$_2$ and TiO$_2$ after exposing to the NO+O$_2$ mixture for 40 min at 200 and 300 °C. Conditions: NO = 1500 ppm, O$_2$ = 10%.



**Fig. 4.** DRIFTS spectra of adsorbed species over Au/TiO$_2$ after exposing in a flow of C$_3$H$_6$ or C$_3$H$_6$ + O$_2$ for 40 min at 200 °C in comparison with the TiO$_2$. Conditions: C$_3$H$_6$ = 1500 ppm, O$_2$ = 0 or 10%.

The DRIFTS spectra of surface species recorded after 40 min in the flow of C$_3$H$_6$/O$_2$ at different temperatures over Au/TiO$_2$ are shown in Fig. 3, in which assignment of the absorbance bands was listed in Table 1. The observable oxygenated hydrocarbons were formate (2956, 2875, 1550, and 1381 cm$^{-1}$), acetate (2986, 2936, 1550, and 1440 cm$^{-1}$), and acetone (2986, 2936, and 1675 cm$^{-1}$). The presence of acetone on the catalyst surface was only detected until 250 °C. The intensity of formate band at 2875 cm$^{-1}$ was increased when the temperature rose upto 250 °C, then it decreased. Thus the amount of adsorbed formate species was reduced at high temperature after reaching the maximum at 250 °C. On the other hand, intensity of acetate band at 1440 cm$^{-1}$ was
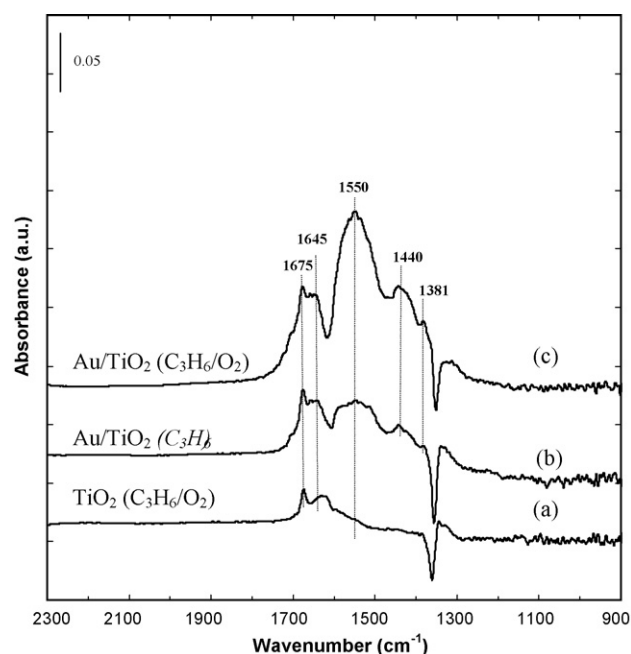
increased as elevating temperature and remained strong at very high temperatures (300–400 °C). Band at 1645 cm$^{-1}$ was assignable to adsorbed H$_2$O. The appearance of this band indicated that the total oxidation of C$_3$H$_6$ by O$_2$ was occurred.

The role of nano Au particles in the formation of oxygenated hydrocarbons may be deduced from the difference in the spectra shown in Fig. 4. The spectra (a) and (c) were recorded at 200 °C over TiO$_2$ and Au/TiO$_2$ after 40 min in a flow of C$_3$H$_6$/O$_2$ (a and c). The spectrum (b) was obtained over Au/TiO$_2$ after exposing in an O$_2$-free stream. During C$_3$H$_6$/O$_2$/He exposure, only weak band of acetone (1675 cm$^{-1}$) was obtained on the support TiO$_2$ comparing to the much stronger bands of acetate (1550, 1444 cm$^{-1}$), formate
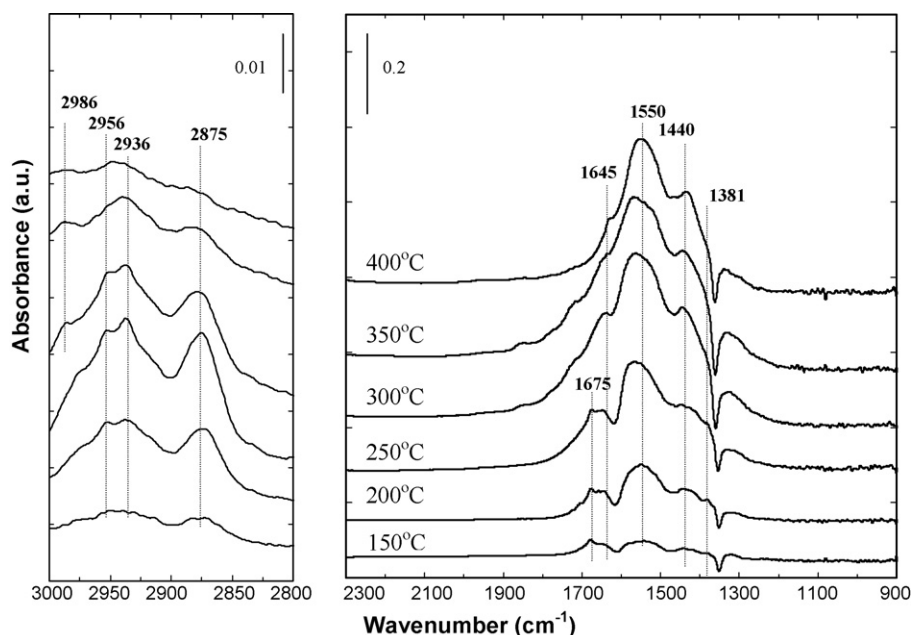


**Fig. 3.** DRIFTS spectra of adsorbed species over Au/TiO$_2$ after exposing in flow of C$_3$H$_6$ + O$_2$ for 40 min at different temperatures. Conditions: C$_3$H$_6$ = 1500 ppm, O$_2$ = 10%.
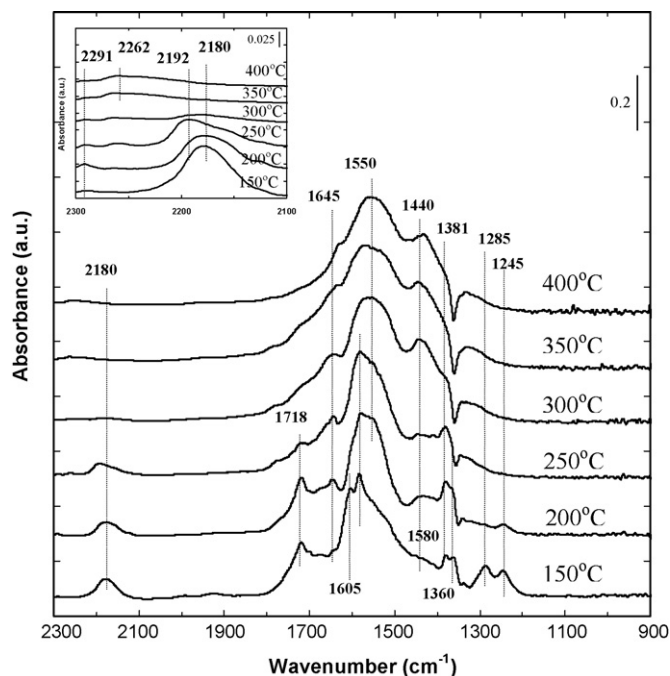
**Fig. 5.** DRIFTS spectra of adsorbed species over Au/TiO$_2$ after 40 min in flows of NO + C$_3$H$_6$ + O$_2$ at different temperatures. Conditions: NO = 1500 ppm, C$_3$H$_6$ = 1500 ppm, O$_2$ = 10%.

(1550, 1381 cm$^{-1}$), and acetone (1675 cm$^{-1}$), on the Au/TiO$_2$. Thus, nano Au particles are essential for the partial oxidation of C$_3$H$_6$ forming oxygenated hydrocarbons. From spectrum (b) of Fig. 4, it is noted that the adsorbed oxygenated species (acetate, formate and acetone) can be formed on Au/TiO$_2$ without O$_2$ existence. In this case, these species might be formed by the reaction between C$_3$H$_6$ and surface (-OH) groups of the support. However, the presence of oxygen led to the more oxygenated hydrocarbons generated on the catalyst's surface as reflected from the stronger intensities obtained in spectrum (b) in comparison with spectrum (c). The lost of TiO$_2$ surface (-OH) groups was observed because of the negative bands around 3715 cm$^{-1}$ (data not shown). Thus, the adsorbed oxygenate species, which formed by the catalysis of Au particles, were probably located on the support sites near Au particles.

### 3.2. Formation of adsorbed species during SCR reaction

The collection of DRIFTS spectra after the Au/TiO$_2$ catalyst was exposed to the reaction mixture (NO/C$_3$H$_6$/O$_2$/He) for 40 min at various temperatures from 150 to 400 °C is shown in Fig. 5.

In the spectral range 1900–900 cm$^{-1}$, adsorbed oxygenated hydrocarbons were acetaldehyde (1718 cm$^{-1}$), acetate (1550, 1440 cm$^{-1}$) and formate (1550, 1381, 1360 cm$^{-1}$). The band of acetaldehyde was observed in the temperature range of 150–250 °C. Acetone band at 1675 cm$^{-1}$, which was observed in the co-adsorption C$_3$H$_6$/O$_2$ (Fig. 3), was not obviously detected in the reaction condition. Additionally, intensities of formate bands (1381, 1360 cm$^{-1}$) were remarkably stronger than those obtained during co-adsorption C$_3$H$_6$/O$_2$ (Fig. 3). Thus, the presence of NO in the gas stream contributes to the increases in amount of oxygenated hydrocarbons, especially acetaldehyde and formate, at low temperatures. However, the spectra in this frequency range of Fig. 5 at higher temperatures (300–400 °C) were almost similar to those obtained in the co-adsorption C$_3$H$_6$/O$_2$ (Fig. 3) at the respective temperatures. Taking the results of co-adsorption NO/O$_2$ (Fig. 1) into account, it is seen that bidentate nitrate (1580, 1285 cm$^{-1}$) was the predominant nitrate species presented on the catalyst surface.
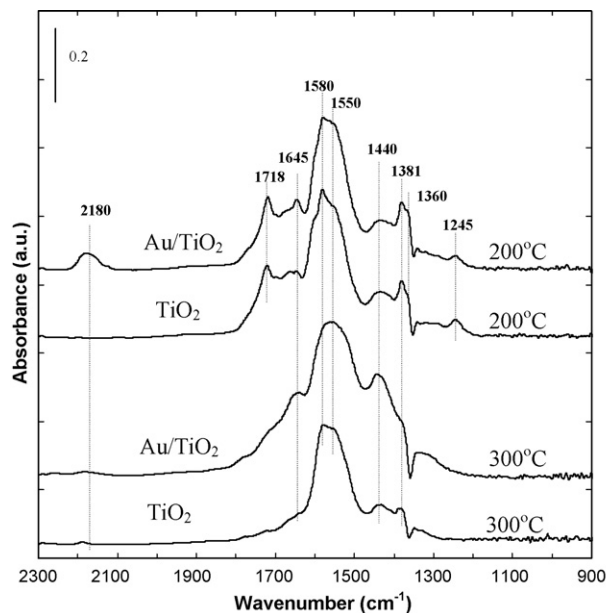


**Fig. 6.** DRIFTS spectra of adsorbed species after 40 min in streams NO + C$_3$H$_6$ + O$_2$ over TiO$_2$ and Au/TiO$_2$ at indicated temperatures. Conditions: NO = 1500 ppm, C$_3$H$_6$ = 1500 ppm, O$_2$ = 10%.

Bridging (1605, 1245 cm$^{-1}$) and monodentate (1517, 1285 cm$^{-1}$) species were only observed at 150 °C. The formation of bridging nitrate became difficult in the presence of C$_3$H$_6$ probably due to the competitive adsorption on the surface active sites.

Importantly, several bands were observed only in the reaction conditions in the wavenumber range of 2300–2100 cm$^{-1}$. These bands are attributed to cyanide (-CN) (2291–2262 cm$^{-1}$), and isocyanate (-NCO) (2192–2175 cm$^{-1}$) compounds. They have been considered as important intermediates of the SCR of NO by hydrocarbons [1]. These bands were observed obviously in 150–300 °C. However, the spectra obtained at different reaction times indicated that the intensity of (-NCO) band, not (-CN), was gradually increased when the reaction time was increased. The intensity of (-NCO) bands were reduced when the temperature was increased. The (-NCO) bands were not detected at very high temperatures (350, 400 °C). Over Au/Al$_2$O$_3$ catalyst, however, bands of these species, especially (-NCO), were strongly detected at higher temperatures (between 350 and 450 °C) and they disappeared at temperature above 500 °C [8]. Consistently, high catalytic activity of Au/Al$_2$O$_3$ was obtained at relatively higher temperatures than that of Au/TiO$_2$ [3,5–7].

The differences of surface species formed during SCR reaction on the TiO$_2$ and Au/TiO$_2$ are shown in Fig. 6. At 200 °C, the observed bands in the region 1900–900 cm$^{-1}$ were similar over both samples, except the intensity of band of adsorbed H$_2$O (1645 cm$^{-1}$) which was much higher in the case of Au/TiO$_2$. On the TiO$_2$ support, unlike the results in co-adsorption C$_3$H$_6$/O$_2$ (Fig. 4), adsorbed oxygenated hydrocarbons such as acetate, formate, acetaldehyde can be strongly detected during the C$_3$H$_6$/O$_2$/NO exposure. Thus, these species were formed with the presence of NO in the gas stream by active sites on TiO$_2$. However, at this temperature a significant difference between TiO$_2$ and Au/TiO$_2$ was the (-NCO) band at 2180 cm$^{-1}$. This band was only strongly observed on Au/TiO$_2$. Therefore, nano-sized Au particles were crucial to the formation of these key intermediates.

Comparative results at 300 °C indicated that band of acetate (1440 cm$^{-1}$) on Au/TiO$_2$ was significantly stronger than that on TiO$_2$ as seen from Fig. 6. Therefore, the presence of nano-sized Au particles accelerates the formation of surface acetate species. More-
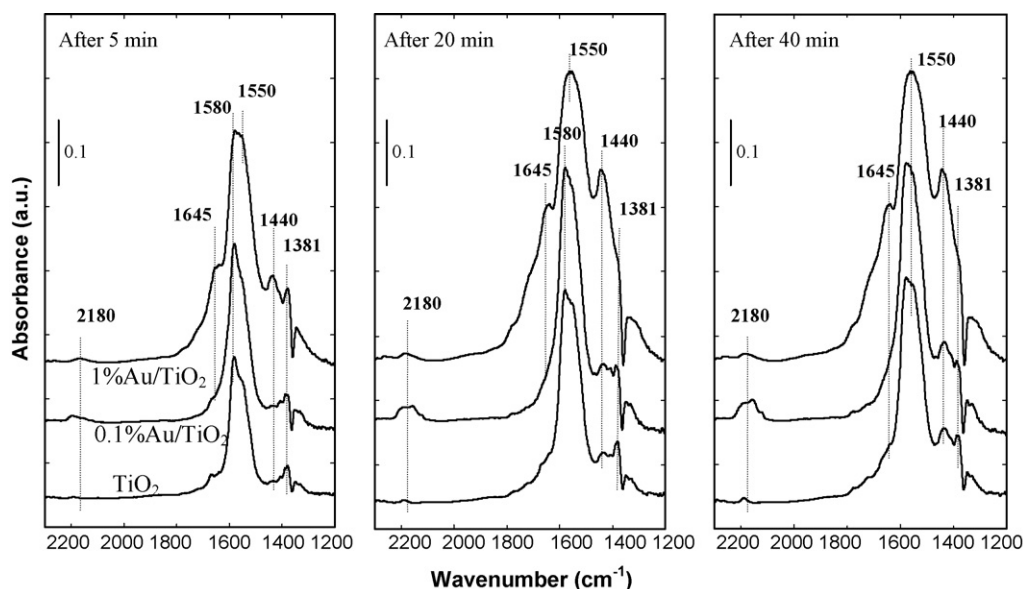
**Fig. 7.** Dynamic change of DRIFTS spectra of adsorbed species in streams NO + C$_3$H$_6$ + O$_2$ over TiO$_2$, 0.1%Au/TiO$_2$ and 1%Au/TiO$_2$ at 300 °C. Conditions: NO = 1500 ppm, C$_3$H$_6$ = 1500 ppm, O$_2$ = 10%.

over, although the intensities of (–NCO) bands were almost similar in both samples at 300 °C but the origins may be different. The low intensity of (–NCO) band in Au/TiO$_2$ may be originated by the fast conversion of these intermediates to N$_2$. Contrarily, hardly forming (–NCO) on TiO$_2$ without the presence of nano Au particles led to the low intensity of the band.

The dynamic changes in DRIFTS spectra of surface adsorbed species during the reaction stream NO/C$_3$H$_6$/O$_2$ at 300 °C over TiO$_2$ and Au/TiO$_2$ (1 or 0.1 wt.% Au) were shown in Fig. 7. The spectra were recorded after 5, 20, and 40 min. It is seen that after 5 min (–NCO) species (2180 cm$^{-1}$) were obviously observed on 1%Au/TiO$_2$ and 0.1%Au/TiO$_2$. The intensity of the band was almost similar in both samples. However, while intensity of (–NCO) band on 1%Au/TiO$_2$ was nearly unchanged until 40 min, that

on 0.1%Au/TiO$_2$ kept increasing. It suggests that the accumulation of (–NCO) compounds was observed on 0.1%Au sample, but not on 1%Au sample. Therefore, nano-sized Au particles contributed to the conversion of (–NCO) intermediates possibly to N$_2$.

### 3.3. Consumption of adsorbed species

The consumption of adsorbed oxygenated hydrocarbons (acetone, acetate and formate) is shown in Figs. 8 and 9. The Au/TiO$_2$ sample was first exposed to C$_3$H$_6$/O$_2$ stream for 40 min then purged by He for 20 min, and finally flowed NO/O$_2$. In the region (2300–1200 cm$^{-1}$), the reduction of acetone band at 1675 cm$^{-1}$ was obviously observed in the results at 200 and 250 °C of Fig. 8.



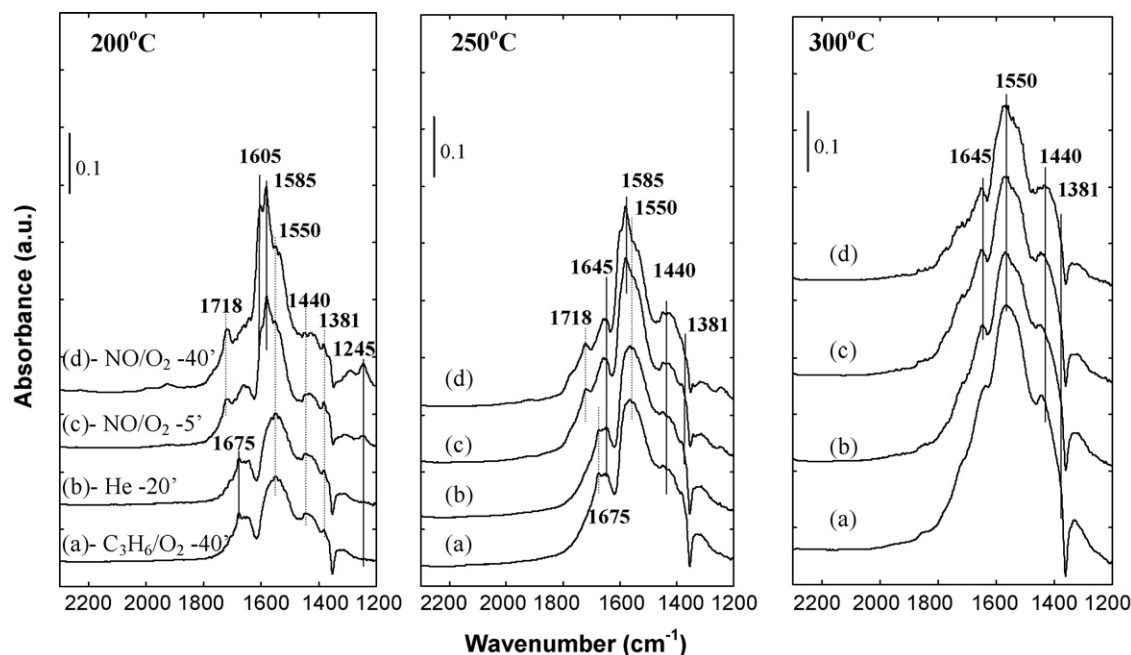**Fig. 8.** DRIFTS spectra in the range (2300–1200 cm$^{-1}$) recorded over Au/TiO$_2$ after flowing of C$_3$H$_6$ + O$_2$ for 40 min (a) followed by purging He for 20 min (b), then flowing of NO + O$_2$ (c and d) at the indicated temperatures and times.

**Fig. 9.** DRIFTS spectra in the C–H stretching region and (–NCO) bands recorded over Au/TiO$_2$ after flowing of C$_3$H$_6$ + O$_2$ for 40 min (a) followed by purging He for 20 min (b), then flowing of NO + O$_2$ (c and d) at the indicated temperatures and times.

Simultaneously, band of acetaldehyde at 1718 cm$^{-1}$ was appeared which may imply that the conversion of acetone to acetaldehyde was occurred at those temperatures. Some research groups proposed the important role of aldehydes such as acetaldehyde and formaldehyde in the formation of (–NCO) [27,28]. However, the observation over Au/TiO$_2$ did not follow this proposal since (–NCO) band (2180 cm$^{-1}$) was not detected even though the acetaldehyde band (1718 cm$^{-1}$) was strongly recorded. Furthermore, although acetate and formate bands (1550, 1440, 1381 cm$^{-1}$) were almost unchanged at those temperature, these bands were

significantly decreased at 300 °C. It indicated that the adsorbed formate and acetate were rapidly consumed in the flow of NO/O$_2$ at 300 °C.

The changes of adsorption bands in the (C–H) stretching region (3000–2800 cm$^{-1}$) at 200, 250, and 300 °C are reported in Fig. 9. It should be noted that, the band at 2936 cm$^{-1}$ can attribute to both acetone and acetate. At 200–250 °C, the decrease of this band together with band at 1675 cm$^{-1}$ (acetone, Fig. 8) and the appearance of acetaldehyde band at 1718 cm$^{-1}$ (Fig. 8) suggested that the 2936 cm$^{-1}$ band is assigned to acetone at these temper-



**Fig. 10.** DRIFTS spectra recorded over Au/TiO$_2$ after flowing of NO + O$_2$ for 40 min (a) followed by purging He for 20 min (b), then flowing of C$_3$H$_6$ + O$_2$ (c and d) at the indicated temperatures and times.
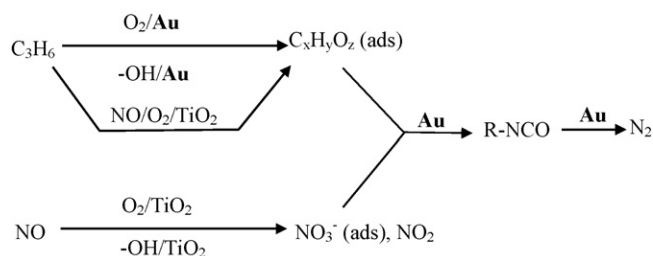
**Fig. 11.** Schematic diagram of reaction mechanism over Au/TiO$_2$ catalyst.

atures. The reduction of formate bands (2954, 2875 cm$^{-1}$) were insignificant at 200, 250 °C. Therefore, formate species were considerably stable at low temperatures. However they were rapidly reduced at 300 °C, even after He purge. In this spectral region, acetate bands (2986, 2936 cm$^{-1}$) were strongly observed only at 300 °C. At this temperature, band at 2936 cm$^{-1}$ is attributed to acetate since almost no acetone presented (Fig. 8). Acetate bands were gradually reduced under the flowing of NO/O$_2$. Therefore, both adsorbed acetate and formate were reactive compounds over Au/TiO$_2$ catalyst. This observation is different with some other Al$_2$O$_3$ supported catalysts in which acetate species were reactive compounds and formate species were considered as spectator [29,30].

Importantly, *–NCO) band, which was at 2175 cm$^{-1}$ (200, 250 °C) or shifted to 2205 (300 °C), was weakly detected at the three temperatures (Fig. 9). The band was observed at the early time of flowing NO/O$_2$ (1 and 2 min). However, they were rapidly reduced and disappeared especially at 300 °C. Interestingly, when using NO$_2$ instead of NO/O$_2$ at 300 °C, the (–NCO) band was observed until 40 min exposure (data not shown). Therefore, the interaction of adsorbed oxygenates with nitrate (formed from NO/O$_2$) and/or NO$_2$ produces the (–NCO) key intermediates.

For investigation of the consumption of adsorbed nitrate species, the Au/TiO$_2$ sample was first exposed to NO/O$_2$ stream for 40 min then purged by He for 20 min, and finally flowed C$_3$H$_6$/O$_2$. The spectra obtained at 200, 250, and 300 °C are shown in Fig. 10. At 200 °C, intensities of nitrate bands (1605, 1585, and 1245 cm$^{-1}$) were almost unchanged after the sample was exposed to C$_3$H$_6$/O$_2$ for 40 min. Hence, the nitrate species were too stable to be released from the catalyst surface at the low temperature. Oxygenated hydrocarbons detected in the spectra were acetone (1675 cm$^{-1}$), formate (1380 cm$^{-1}$), and acetate (1440 cm$^{-1}$), which were similar to those obtained in the co-adsorption C$_3$H$_6$/O$_2$ (Fig. 3). Moreover, acetaldehyde band (1718 cm$^{-1}$) was not detected in these experiments although an abundance of nitrate species on the catalyst surface. Thus, the gas phase NO$_x$ is needed to form this compound. Additionally, the (–CN) or (–NCO) bands were not detected during these measurements. Since adsorbed nitrate species were stable at low temperatures and only small amount presented at high temperatures (Fig. 10), it was difficult for the interaction of the adsorbed nitrate and the adsorbed oxygenated hydrocarbons to occur on the Au sites.

### 3.4. Discussion of reaction mechanism

In the co-adsorption NO/O$_2$ on Au/TiO$_2$, nitrate (bridging nitrate, bidentate nitrate, and monodentate nitrate) was observed depending on the temperature (Fig. 1). When the temperature was increased, the monodentate nitrate was no longer detected and the intensities of IR bands ascribed to bridging and bidentate nitrate were quickly decreased indicating the reduction in the amount of nitrate species on the catalyst surface. On the other hand, during the co-adsorption C$_3$H$_6$/O$_2$, the surface oxygenated hydrocarbons

detected are mainly acetate, formate, and acetone (Fig. 3). Adsorbed H$_2$O was detected during exposing the sample to C$_3$H$_6$/O$_2$ suggesting the occurrence of the total oxidation of C$_3$H$_6$. Although nano-sized Au particles did not contribute to the formation of adsorbed nitrate (Fig. 2), they played an important role in the partial oxidation of C$_3$H$_6$ to produce acetate and formate in the co-adsorption C$_3$H$_6$/O$_2$ (Fig. 4). Weak band of acetone was observed on TiO$_2$ during the flowing of C$_3$H$_6$/O$_2$ at 200 °C while strong bands of carbonxylates (formate, acetate) and also acetone were recorded over Au/TiO$_2$. Hence, The presence of Au nano-sized particles was essential for the formation of acetate, formate and acetone. The species were then adsorbed probably on adjacent active sites of the support or at the interface.

In SCR reaction (NO/C$_3$H$_6$/O$_2$), the appearance of acetaldehyde, cyanide (–CN) and isocyanate (–NCO) species were observed on the catalyst surface besides nitrate, acetone, acetate, formate. The conversion of acetone to acetaldehyde by a reaction with gaseous NO$_x$ may occur on TiO$_2$ sites. Unlike the co-adsorption C$_3$H$_6$/O$_2$ condition, the active sites of TiO$_2$ may contribute to the formation of formate in the reaction condition. However, as shown in Fig. 6 acetate band (1440 cm$^{-1}$) observed at 300 °C was significantly stronger over Au/TiO$_2$ than that over TiO$_2$. Therefore, the presence of Au was still necessary for acetate formation. Importantly, nano-sized Au particles were crucial for the formation of the key intermediates (–CN, and –NCO). It is obviously realized that a strong band of (–NCO) at 2180 cm$^{-1}$ was recorded over Au/TiO$_2$, but not TiO$_2$, at 200 °C in the reaction condition (Fig. 6). Additionally, DRIFTS results shown in Fig. 7 implied that (–NCO) band was clearly observed on a very low Au-containing sample (0.1%Au/TiO$_2$). Therefore, Au sites are crucial for the formation of these compounds.

Moreover, the difference in the accumulation of (–NCO) species at 300 °C between 1%Au/TiO$_2$ and 0.1%Au/TiO$_2$ suggested the important role of Au in the conversion of (–NCO) intermediate, possibly to N$_2$. The intensity of the (–NCO) band was almost stable after 5 min reaction over 1%Au/TiO$_2$ while it continued to increase until 40 min reaction over 0.1%Au/TiO$_2$ (Fig. 7). Thus, Au sites may participate in the conversion of (–NCO) species which resulted in the prevention of (–NCO) accumulation over the high Au loading sample. The conversion of (–NCO) intermediates may produce NH$_3$ as observed over Ag/Al$_2$O$_3$ [31], and Rh/TiO$_2$ [27]. However, over Au/TiO$_2$ catalyst, the (N–H) stretching band of NH$_3$ at 3141 and 3048 cm$^{-1}$ [27] were not detected in all of our DRIFTS spectra. Therefore, it is possible that NH$_3$ was not formed over Au/TiO$_2$ catalyst or NH$_3$ was formed then immediately converted to N$_2$.

Additionally, in the investigation of consumption of adsorbed oxygenated hydrocarbons implied that the (–NCO) intermediates were generated by the interaction of adsorbed oxygenates and adsorbed nitrate or/and NO$_2$. Moreover, the DRIFTS results indicated that it is difficult to release adsorbed NO$_3^-$ (bidentate and bridging) from the catalyst surface at low temperature (200 °C).

In summary, a scheme of proposed reaction mechanism on Au/TiO$_2$ is illustrated in Fig. 11. The first step of the SCR by C$_3$H$_6$ over Au/TiO$_2$ catalyst comprises the formation of adsorbed oxygenated hydrocarbons (acetate, formate, acetone, and acetaldehyde) and adsorbed nitrate (monodentate, bidentate, and bridging) on the catalyst surface. The Au active sites are mainly responsible for the formation of acetate species. The interaction between oxygenates and nitrate and/or NO$_2$ produces (–NCO) compounds as the key intermediates. The (–NCO) compounds then converted to N$_2$ and other products as being proposed in literature for Al$_2$O$_3$ supported catalysts [1,32]. Nano-sized Au particles were crucial for the formation of (–NCO) compounds and contributed to following step, the conversion of (-NCO) to N$_2$.

## 4. Conclusions

The formation and consumption of oxygenated hydrocarbons and nitrate species during the SCR by $C_3H_6$ over nano-sized Au/TiO$_2$ catalyst were investigated using in situ DRIFTS. The amount and types of nitrate (bridging, bidentate, and monodetate) were observed on the catalyst surface depending on the temperature. Oxygenated hydrocarbons detected in DRIFTS measurement were mainly acetate, formate, acetone, and acetaldehyde. Over Au/TiO$_2$ catalyst, the interaction of adsorbed oxygenated hydrocarbons and nitrate and/or NO$_2$ produced nitrogen-containing intermediate compounds such as detectable (−CN) and (−NCO) compounds which then possibly converted to N$_2$ and other products. Presence of nano-sized Au particles was necessary to form oxygenated hydrocarbons, especially acetate species, and crucial to the production of (−NCO) intermediate compounds. They also contributed to the conversion of (−NCO) compounds to N$_2$.

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